Electronic Supplementary Information (ESI):

# A separator coated with commercial $LiFePO_4$ and conductive carbon for Li-S battery of good cycling performance

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## Materials

All of the chemicals mentioned in the steps were used directly. LFP was purchased from Shanghai Macklin Biochemical Co., Ltd. Commercial separators (DKJ-14) were purchased from Zhejiang DKJ New Energy Tech Co., Ltd. Anodes were purchased from Tianjin Zhongneng Lithium Industry Co., Ltd. Electrolytes (LS-009) were purchased from DodoChem Co., Ltd. Super P was purchased from Tmall. Ltd. The carbon-coated Al foil was purchased from Guangdong Canrd New Energy Technology Co., Ltd. Carbon black (CB), bisfluoromethane-sulfonimide lithium salt (LITFSI), *N*-methyl pyrrolidone (NMP), *N*, *N*-dimethylformamide (DMF), polyvinylidene difluoride (PVDF), sublimed sulfur (S), carbon nanotubes (CNTs), 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), lithium nitrate ($LiNO_3$), carboxymethyl cellulose (CMC) and lithium sulfide ($Li_2S$) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd.

## Preparation of $Li_2S_6$ solution and electrolyte

Based on the reaction equation (1):

$$Li_2S + 5S \rightarrow Li_2S_6 \quad \text{(S1)}$$

The $Li_2S_6$ solution (0.2 M) was obtained by dissolving S (1.6 g) and $Li_2S$ (0.46 g) in DME (50 ml).

The LiTFSI (1 M) and $LiNO_3$ (0.2 M) were dissolved in a mixed organic solvent of DOL and DME (volume ratio of 1: 1) to obtain a blank electrolyte.

S (320 mg) and $Li_2S$ (92 mg) were dissolved in the blank electrolyte (10 ml) to obtain the $Li_2S_6$ electrolyte (0.2 M).

## Preparation of modified material pieces

The modified material pieces were prepared according to our previous report. [1] DMF was added into LFP-PVDF and stirred evenly, then coated on the aluminum foil. LFP pieces were obtained after vacuum drying (60 ℃). Super P was added to the NMP dissolved with PVDF and stirred evenly, coated on the LFP pieces, and vacuum dried (60 ℃) to obtain LFP-SP pieces. All of the pieces were cut into 15 mm pieces before use.

## Materials characterization

The X-ray diffraction analysis (Smart Lab3KW, XRD) was used to test the crystalline phase of the materials. The scanning electron microscope (Phenom ProX, SEM) was used to observe the micromorphology of the samples. The UV and visible spectrophotometer (UV-2600) was used to test the $Li_2S_6$ solution adsorbed by modified materials. Record contact angles were tested by a contact angle meter (Kino).

## Electrochemical measurements

The electrochemical workstation (Chenhua, CHI760e) was used to test the cyclic voltammetry (CV) and AC impedance (EIS, $10^{-2}$~$10^{5}$ Hz). Through the EIS of the cell (25~95 ℃), the ionic conductivity and activation energy could be calculated. The battery test system (LAND CT2001A, Wuhan, China) was used to test the voltage profiles of lithium symmetric cells and electrochemical performance (cycle and rate performance) of the CR2025 type coin cells.

## Calculation

According to equation (2), the ionic conductivity can be calculated.

$$\sigma = L / (R_b \times A) \quad \text{(S2)}$$

In the equation, $\sigma$ is ionic conductivity, L is the thickness of separators, $R_b$ is the bulk resistance, and A is the contact area between the stainless steel sheet and the separator.

According to Arrhenius equation (3), the activation energy can be calculated.

$$\sigma = A \exp(-E_a / RT) \quad \text{(S3)}$$

In the equation, A is the pre-exponential factor, $E_a$ is the activation energy, and R is the perfect gas constant.

The $Li^+$ diffusion coefficients can be calculated by the Randles Sevcik equation (4).

$$I_P = 2.69 \times 10^5 n^{1.5} A D_{Li^+}^{0.5} C_{Li} V^{0.5} \quad \text{(S4)}$$

In the equation, Ip is the peak current, n is the number of electron transfers, A is the contact area, $D_{Li^+}$ is the $Li^+$ diffusion coefficient, $C_{Li}$ is the concentration of $Li^+$ in an electrolyte, and V is the scanning speed.

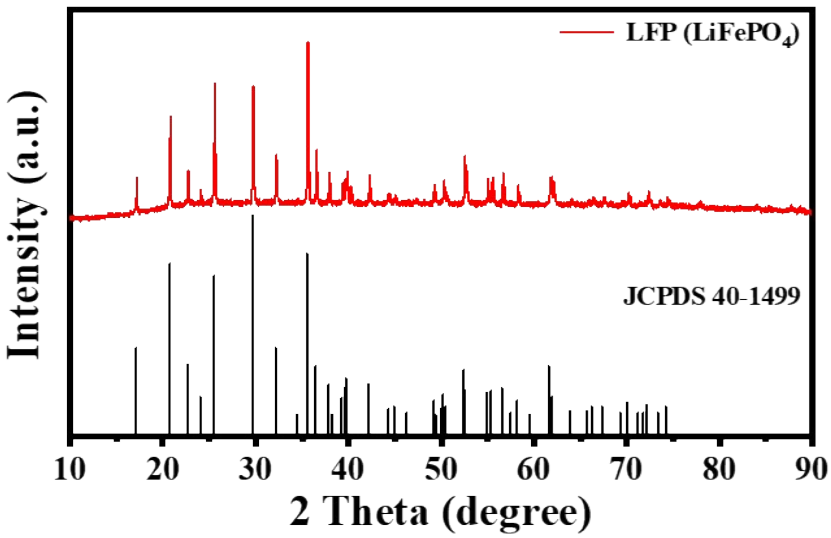


Figure S1. The XRD of LFP.

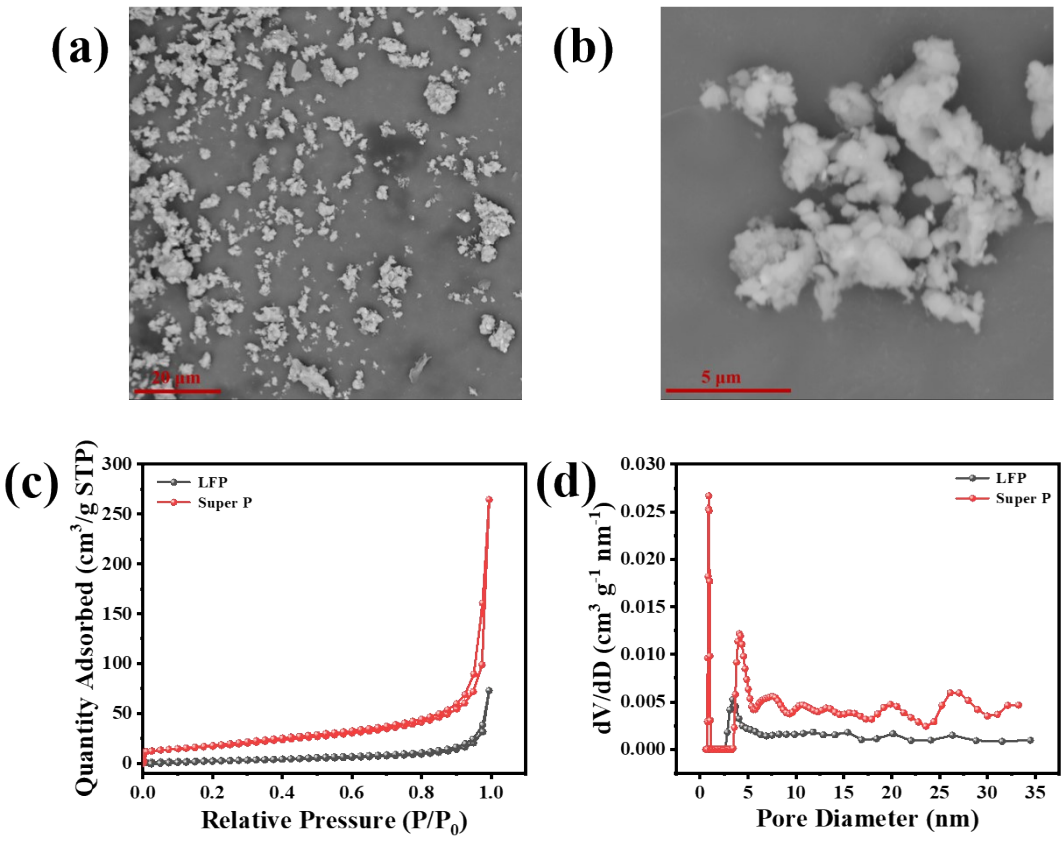


Fig. S2. (a, b) The SEM images of the commercial LFP, (c) Nitrogen adsorption-desorption isotherms and (d) the pore size distributions of the different materials.

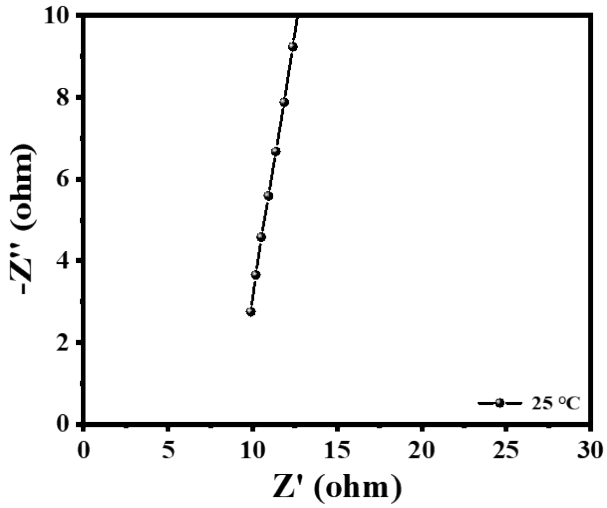


Figure S3. The EIS plot of pure LFP pellet in the SS//SS symmetric cell (25 °C).

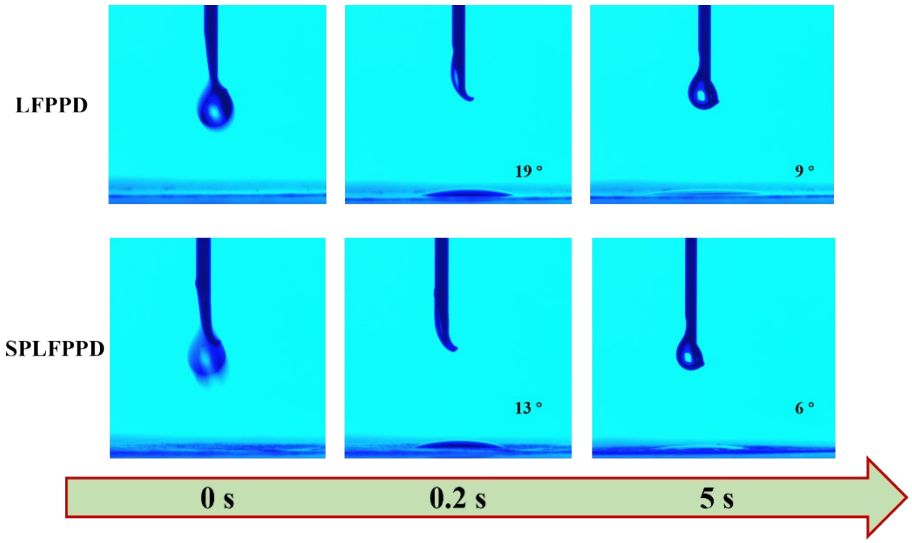


Figure S4. Contact angle tests for the separators.

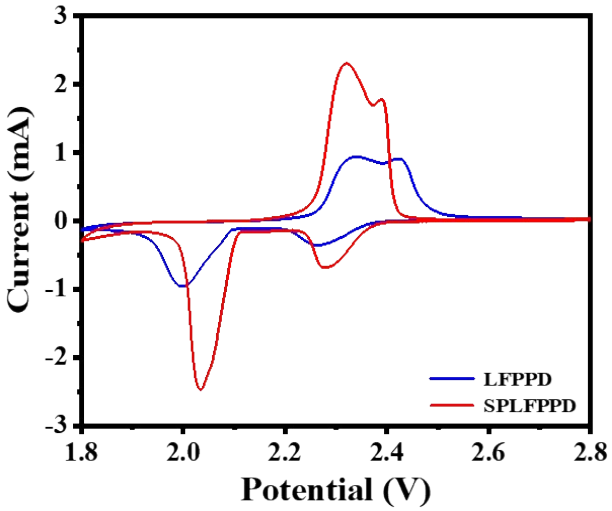


Figure S5. CV curves of the Li-S cells at 0.1 mV $s^{-1}$ for the first cycle.

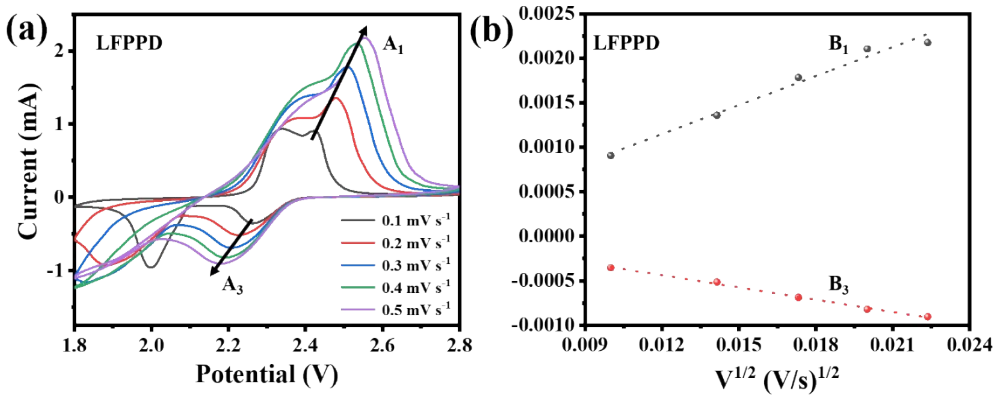


Figure S6. The CV curves of the cell with (a) the LFPPD at different scan rates and (b) the corresponding linear matching of peak point currents.

Table S1. $Li^+$ diffusion coefficients of the Li-S cells with different separators.

| Separators | $D_{Li^+}$($cm^2$/s)-anodic peak around 2.5 V | $D_{Li^+}$($cm^2$/s)-cathodic peak around 2.0 V | $D_{Li^+}$($cm^2$/s)- cathodic peak around 2.3 V |
|---|---|---|---|
| LFPPD | $1.3\times10^{-8}$ | - | $2.3\times10^{-9}$ |
| SPLFPPD | $5.6\times10^{-8}$ | $1.7\times10^{-8}$ | $6.3\times10^{-9}$ |

Table S2. EIS parameters of the equivalent circuit simulation for the cells.

| Cycle number | Resistance (Ω) | SPLFPPD | LFPPD |
|---|---|---|---|
| Before cycling | $R_S$ | 9.6 | 4.6 |
| | $R_{SEI}$ | - | 15.1 |
| | $R_{CT}$ | 11.5 | 52.9 |
| 100 cycles | $R_S$ | 6.1 | 7.1 |
| | $R_{SEI}$ | 8.5 | 27.4 |
| | $R_{CT}$ | 3.0 | 26.6 |

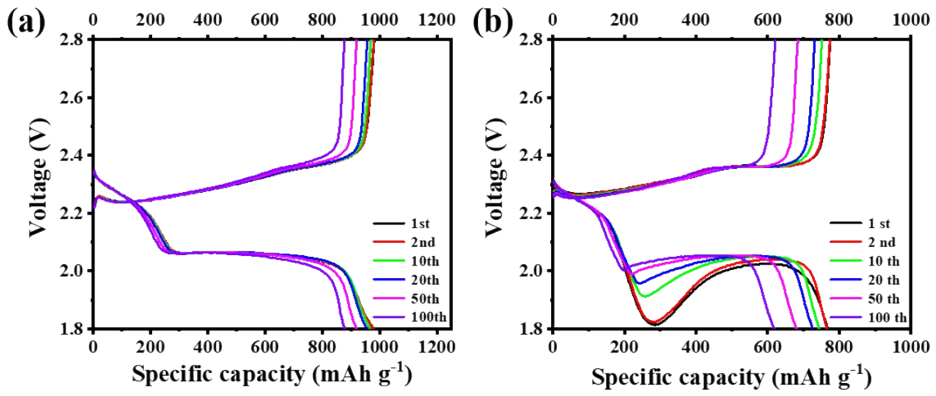


Figure S7. Charge/discharge profiles with the (a) SPLFPPD and (b) LFPPD at 1 C.

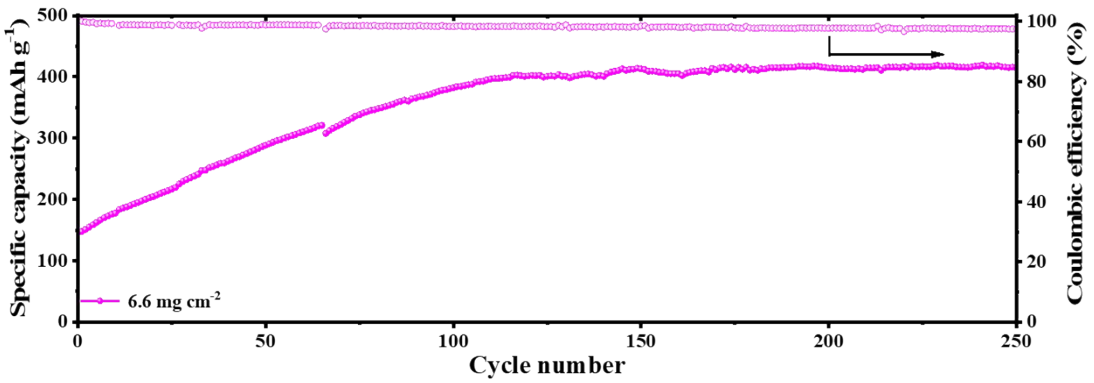


Figure S8. Cycling performance of the Li-S cell with the SPLFPPD under 6.6 mg $cm^{-2}$ at 0.2 C after activation.

Table S3. A comparison of cycling performance with the SPLFPPD and other relevant reports.

| Cathode | Separator | S loading (mg $cm^{-2}$) | Initial capacity (mAh $g^{-1}$) | Cycle number | Decay rate per cycle (%) | Ref. |
|---|---|---|---|---|---|---|
| **S/CNT** | **SPLFPPD** | **~1.0** | **980<br>723** | **800 (1 C)<br>1000 (5 C)** | **0.062<br>0.045** | **This work** |
| S/GO | Asy-PP/Li-Mg | 1.0-1.3 | 1116 | 400 (1 C) | 0.07 | 1[2] |
| S/C | $MoS_2$ | NA | 808 | 600 (0.5 C) | 0.083 | 2[3] |
| S/C | $SrF_2$-G/PP | NA | NA | 300 (0.5 C) | 0.07 | 3[4] |
| S/C | $VN_{1-x}$@V-NC@PP | 1.5 | NA | 500 (2 C) | 0.071 | 4[5] |
| S/C | Fe/Co-N-HPC /PP | 2.1 | 977 | 300 (1 C) | 0.109 | 5[6] |
| S/KB | MWCNTs/NCQDs/PP | 1.3-1.5 | 1330.8 | 500 (0.5 C) | 0.1 | 6[7] |
| S/super P | SCOF | 1.0 | 772 | 600(1 C) | 0.07 | 7[8] |
| S/super P | PyBBT-COF | 1.0 | 1249 | 100(0.2 C) | 0.27 | 8[9] |
| NA | PCA-TO@PP | 0.8 | 833 | 200(1 C) | 0.19 | 9[10] |
| S/MWCNT | CNF/Co-$Co_9S_8$-NC | 1.5 | 746 | 300(2 C) | 0.083 | 10[11] |

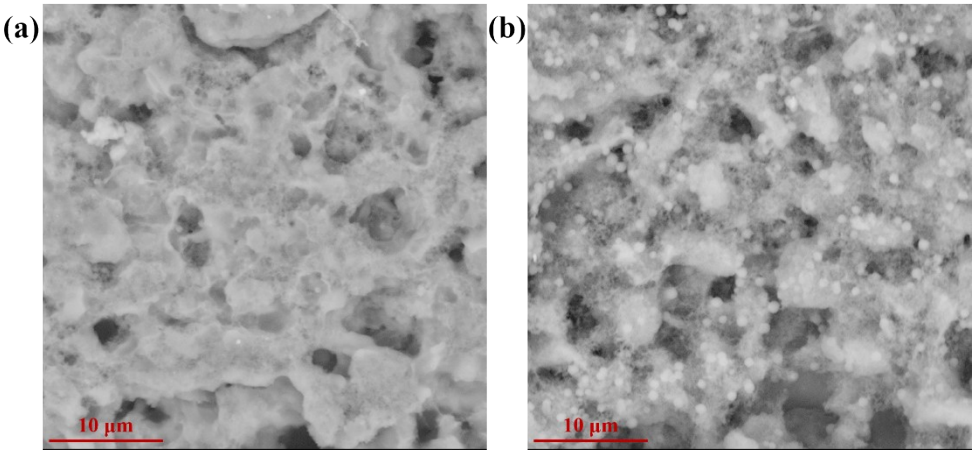


Figure S9. SEM of C-S cathodes. SEM images of Li-S cells with the (a) LFPPD and (b) SPLFPPD after 100 cycles (1 C).

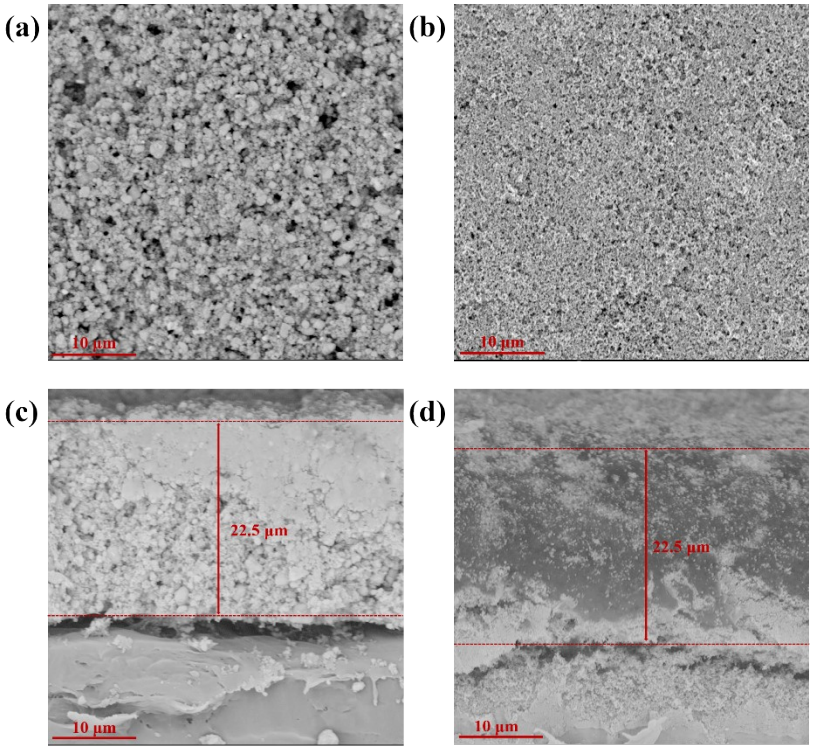


Figure S10. SEM of thick modified separators. The surface of the (a) TLFPPD, (b) TSPLFPPD, and (c), (d) the section of the separators.

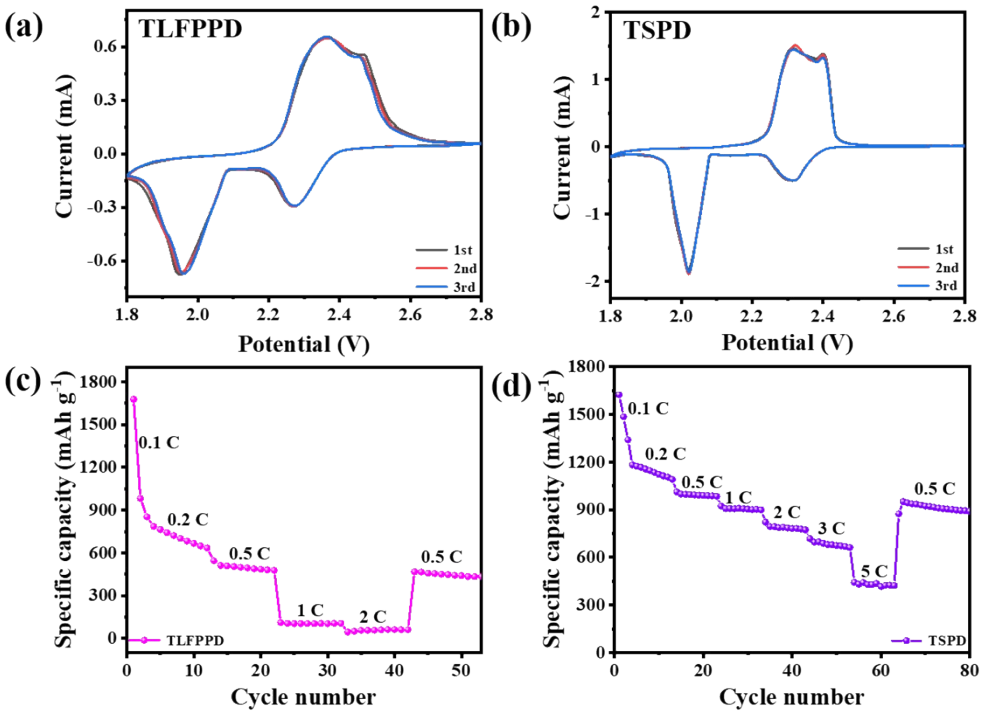


Figure S11. The CV and rate performance tests. The CV curves of the cells with the (a) TLFPPD and (b) TSPD for the first three cycles (0.1 mV $s^{-1}$). The rate performance tests of the Li-S cells with the (c) TLFPPD and (d) TSPD.

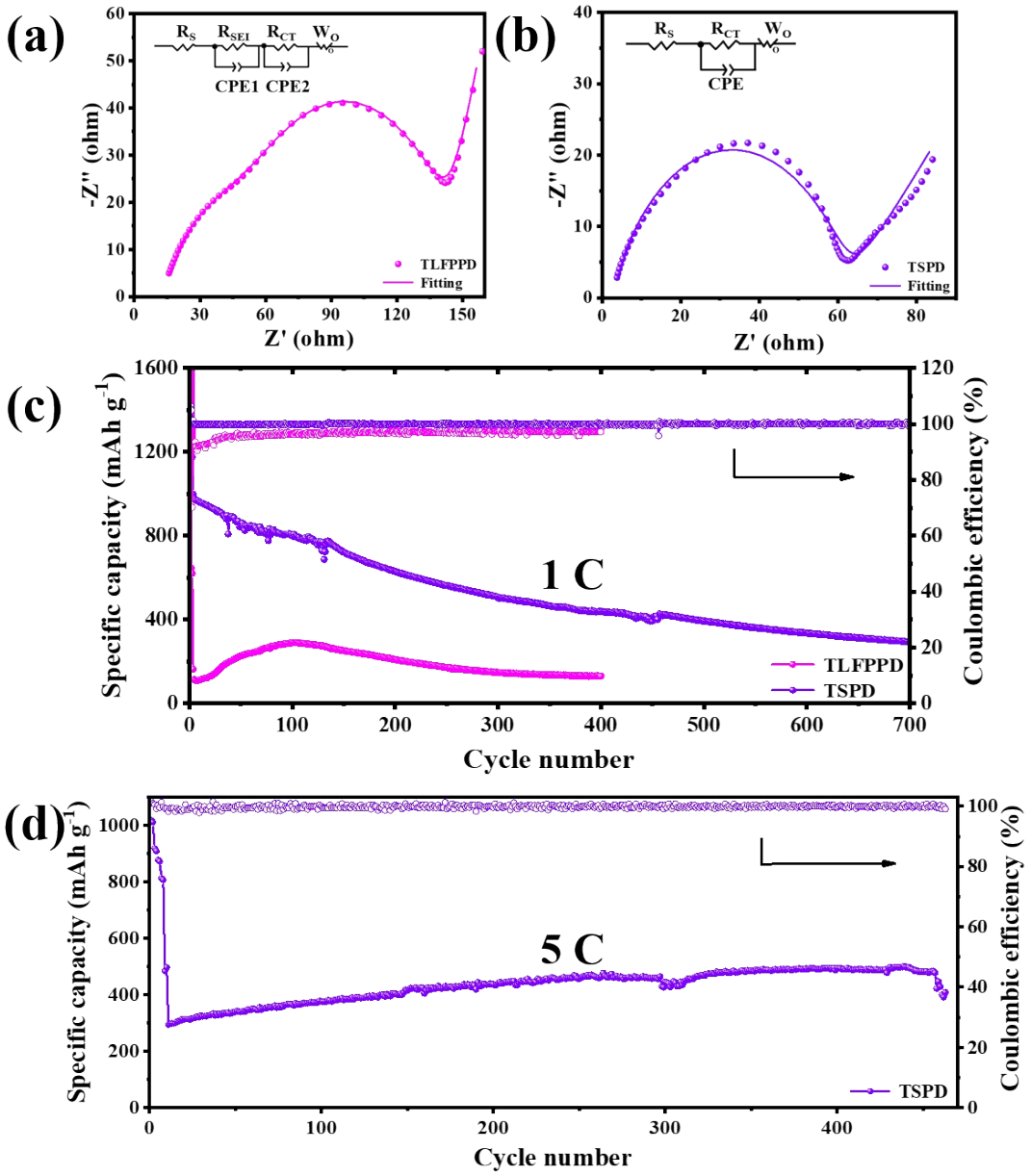


Figure S12. The EIS and cycling performance tests. The EIS tests of the cells with the (a) TLFPPD and (b) TSPD before cycling (insets: equivalent circuit). (c) The cycling performance of the Li-S cells with the TLFPPD and TSPD at 1 C. (d) The cycling performance of the Li-S cells with the TSPD at 1 C.

Table S4. EIS parameters of the equivalent circuit simulation for the cells.

| Cycle number | Resistance (Ω) | TLFPPD | TSPD |
|---|---|---|---|
| Before cycling | $R_S$ | 12.7 | 2.5 |
| | $R_{SEI}$ | 43.1 | - |
| | $R_{CT}$ | 74.5 | 58.8 |

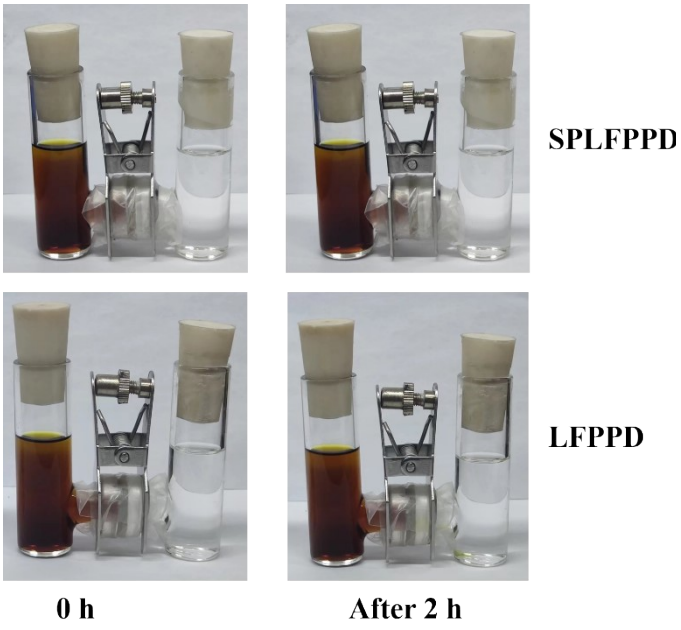


Figure S13. Photographs of polysulfides diffusion test in H-type cells with the LFPPD and SPLFPPD.

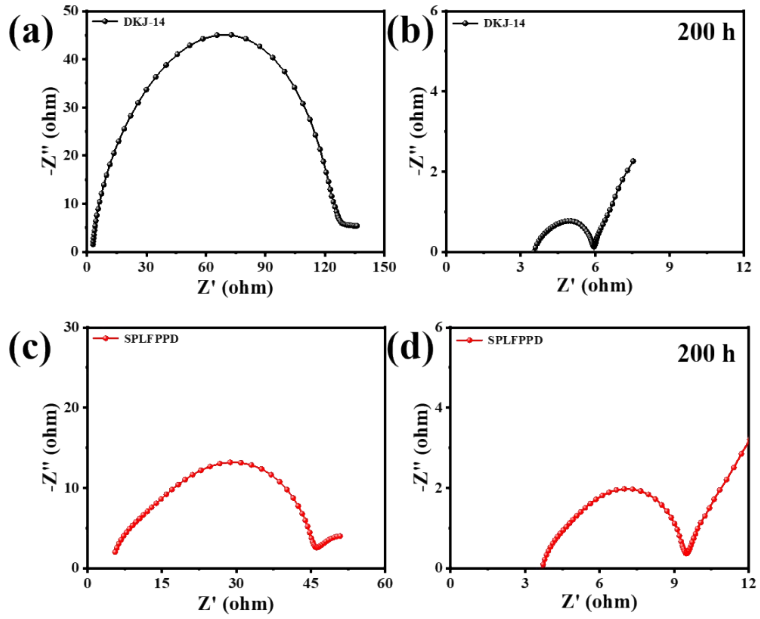


Fig. S14. EIS spectra of the cells with the DKJ-14 and SPLFPPD (a, [12] c) before and (b, d) after 200 hours at 0.5 mA $cm^{-2}$.

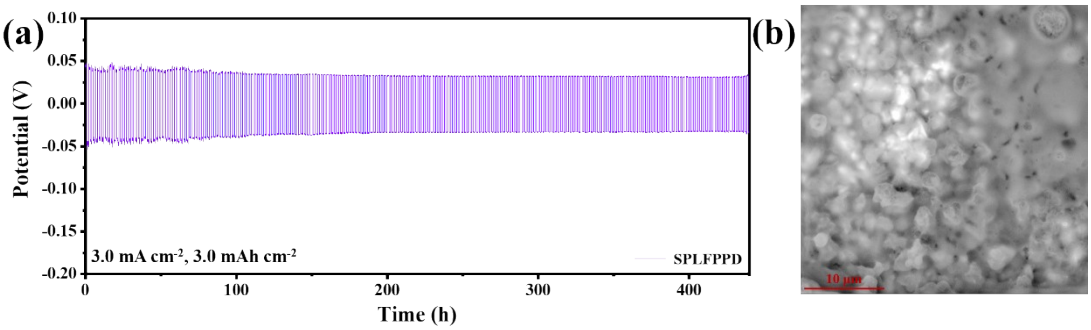


Figure S15. Li stripping/plating behavior and the SEM image. (a) Voltage profiles of the Li//Li cell with the SPLFPPD at 3.0 mA $cm^{-2}$ (3.0 mAh $cm^{-2}$). (b) The lithium-deposited morphologies in Cu foils of Li//Cu cells with the LFPPD at 0.5 mA $cm^{-2}$ (5 h).

## References


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